JAPANESE [JP,06-228824,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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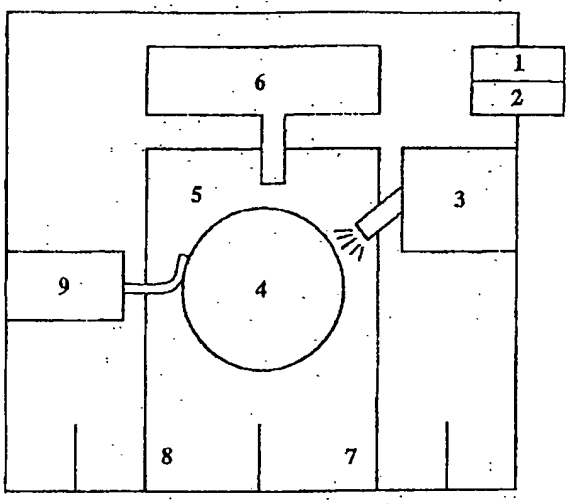
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the purification method of the nanotube using the various technical approaches, such as a column chromatography for separating a carbon nanotube from other carbon matter, ultra-centrifugal separation, and ultrasonic grinding. In new matter called a carbon nanotube, this invention is effective, when manufacturing and using it especially for a field industrial [electric], industrial and.
[0002]
[Description of the Prior Art] Since the carbon nanotube was discovered in 1991 (58 56- Nature, 354, 1991), it is capturing the spotlight in the world as a new ingredient with which various potential application, such as a 1-dimensional thin line and a catalyst, is expected. Recently, we have reported the manufacture approach (Japanese Patent Application No. No. 172242 [four to]) which can compound a arbon nanotube in large quantities.
[0003] if carbon arc discharge is made to cause in the container filled with inert gas -- C, C2, and C3 etc. -- the plasma including a carbon kind occurs. these -- small -- a **** carbon kind -- gradually -- condensing -- soot, fullerene, a nanotube, and a nano particle -- it grows up to be the larger structure of the carbon matter of the solid-state of high density etc. further. We have already shown clearly that the yield of a nanotube is deterministically dependent on the pressure of the inert gas in the reaction container which makes them generate. The yield of a nanotube becomes the highest when the pressure of inert gas is in the range of 500 to 2500torr(s).
[0004]
[Problem(s) to be Solved by the Invention] However, also under optimum conditions, a nano particle is generated with a nanotube and, occasionally generates other carbon matter, such as glassy carbon and amorphous carbon, to coincidence. Therefore, in order to use a nanotube, it is necessary to separate carbon matter other than these nanotubes after composition.
[0005] The method of separating a nanotube from a nano particle and other carbon matter is not reported the place to current.
[0006] This invention aims at obtaining a uniform good nanotube ingredient about discrete quantity, magnitude, and electrical conductivity.
[0007]
[Means for Solving the Problem] This invention is made as a result of a carbon

Drawing selection drawing 1



1．排気装置
2．ガス導入装置
3．電子ビームまたはコロナ放電装置
4．回転ドラム
5．可動部分の制御装置
6．試料室
7．分離試料受け入れ室1
8．分離試料受け入れ室2
9：試料落とし

[Translation done.]

nanotube's examining wholeheartedly that purification and separation are possible by use of techniques, such as a column chromatography, ultra-centrifugal separation, and ultrasonic grinding, and a surfactant.

[0008] Furthermore, by using these approaches, it is possible to short-range-ize the size distribution of a nanotube, and it is possible to separate the nanotube with which electrical conductivity differs.

[0009] When the rough product containing the compounded nanotube is observed with an atomic force microscope (AFM), it turns out that it consists of non-fixed form carbon with which only the nanotube was densely got blocked, such as a bundle-like fiber part, a nano particle, glassy carbon, and amorphous carbon. A detailed thing and since the bundle-like fiber structure of a nanotube is comparatively firm, it cannot be destroyed by the usual dynamic grinding. Ultrasonic grinding is effective in destruction of the bundle-like fiber structure. It is possible to pulverize the bundle-like fiber structure of a nanotube for the frequency of a supersonic wave completely 28kHz, 45kHz, and 100kHz by using three kinds, combining (this fact became clear from observation of AFM). When it is made to distribute ultrasonically in a solvent, even if a surface active agent is used for a nanotube and carbon matter other than a nano particle and it does not carry out them, they can be dissociated from a nanotube and a nano particle only by filtration. In purification of a nanotube, a surfactant carries out special work on the next stairway. If a surface active agent is used, it will become possible to distribute a nanotube and a nano particle completely in a solvent, i.e., to carry out a solvation. If a surface ctive agent is not added, a nanotube (and nano particle) will begin condensation at .ie same time it will once stop supply of a supersonic wave. Therefore, use of a surface active agent is indispensable to solubilization of a nanotube.

[0010] Furthermore, it is possible to carry out nanotube separation from a nano particle by the column chromatography method. Also in this approach, especially the size exclusion column chromatography method a difference of that magnitude separates the matter is effective. Generally the size exclusion column chromatography method is used for separation of biopolymers, such as protein, a nucleic acid, and a saccharide. For the first time, this approach was applied to purification of the nanotube which is the super-microcrystal (however, huge in molecular weight) which consists of only carbon, and the effective thing was proved this time.

[0011] Moreover, the approach by concentration gradient ultra-centrifugal separation uses having the configuration where the nanotube and the nano particle differed from other carbon matter, respectively, magnitude, and specific gravity, and separates each. When it observes by the transmission electron microscope (TEM) and AFM, the needlelike structure of an aspect ratio where a nanotube is big, It is admitted that each component of the rough product by which spherical structure, glassy carbon, and amorphous carbon are compounded for a nano particle with non-.xed form structure and a DC arc electric discharge method has a completely different configuration and magnitude. Moreover, it originates in a difference of each structure and specific gravity also differs (specific gravity **1 7 g-cm -3 of the specific gravity> non-fixed form carbon of the specific gravity> nanotube of a nano particle). It devised applying ultracentrifuge to separating a nanotube from a nano particle and non-fixed form carbon based on these experiment facts, and the effectiveness was proved. Furthermore, it is also possible to separate the nanotube itself with the magnitude by repeating the ultra-centrifugal separation of the separated nanotube several times.

[0012] According to theoretical research, a carbon nanotube becomes a metal or an insulator (large semi-conductor of a band gap) according to whenever [diameter and spiral] (1581 Phys.Rev.Letters 68, 1579- 1992). Then, we devised the technique of the nanotube separation based on the electrical property of a nanotube. This approach uses the difference in the method of electrification of a metal type and insulator type nanotube. That is, the sample containing a nanotube is put on a rotating drum, an exposure or a corona discharge shower is showered over it for an electron beam, and it is made the conditions on which a sample can be charged. If this drum is rotated, since a metal type nanotube cannot be charged, it will be slid down from a drum. Since an insulator type nanotube is in the condition of having been charged, it is drawn by electrostatic force to a drum, and it is not slid down in rotation of a drum. Therefore, this approach is very effective when separating a

metal type nanotube and an insulator type nanotube.
[0013] Furthermore, the thing with high homogeneity to acquire for a good nanotube is indispensable, when using a nanotube industrially. By combining the above-mentioned separation approach, it becomes possible to obtain a uniform good nanotube about molecular weight, magnitude, and electrical conductivity. Therefore, the industrial use price of this invention is very large.
[0014]
[Example]
1) It is Sepharose to the column for separation purification chromatographies of the nanotube by the column chromatography method. It is filled up with C1 (product made from Pharmacia) chromatography gel with ethanol. The sample containing a nanotube and a nano particle is made to suspend by ultrasonic distribution in ethanol, and it lets the suspension solution pass in a column. Then, a nanotube and carbon matter other than a nano particle remain in the gel upper part, and can be finely distributed with a nanotube and a nano particle. A nanotube and a nano particle are developed in gel with a developing solution. And a nanotube is separated from a nano particle by difference of the expansion rate originating in molecular weight and a configuration. Furthermore, the nanotube with which molecular weight differs is separable by using this approach. A part of result is shown in Table 1. Moreover, even if it uses surface active agents, such as sodium dodecyl sulfate (SDS), as a developing solution, using the TOSOH TSKgel cellulose CW or a methanol, and ASETONNADO as a bulking agent of a gel filtration chromatography, a nanotube is separable like the above.
[0015]
[Table 1]

ナノチューブとナノ粒子のカラム・クロマトグラフィによる分離の一例

展開時間の区分（分）	区分に含まれる炭素物質	分子量
0～30	分子量の大きい ナノチューブ	10^{8}以上
30～60	分子量の比較的小さい ナノチューブ	10^{8}以下
60～90	分子量の比較的大きい ナノ粒子	10^{7}以上
90以上	分子量の比較的小さい ナノ粒子	10^{6}以下

[0016] 2) Make ethanol suspend the sample containing the separation purification nanotube nano particle of the nanotube using ultrasonic grinding and a demarcation membrane, and carry out ultrasonic grinding. A glass filter (10 micrometers of apertures) separates preparatorily carbon matter with comparatively big particle diameter other than a nanotube nano particle. Next, it lets the ethanol solution of the obtained nanotube nano particle pass to a membrane filter (product made from Milipore). At this time, the solution with which pore size (aperture) performed membrane separation of a nanotube nano particle using the filter which is 8 micrometers, and was filtered after that first is filtered with the filter whose pore sizes are 3 micrometers, 1.2 micrometers, 0.45 micrometers, and 0.22 micrometers one by one. It is possible to separate alternatively a nanotube (from sub mum to about ten micrometers) and a nano particle (from the diameter of several nm to dozens of nm) by filtration actuation based on this membrane separation of a series of. It describes in Table 2 about the nanotube and nano particle which remained on the demarcation membrane by each actuation. Furthermore, a nanotube with short die length and a long nanotube are also separable. By making fine spacing of the pore size of the filter used for a series of filtration actuation, ** is possible also for more nearly alternative separation.
[0017] As a filter, a microfilter (the Fuji film company make), a membrane filter

(Oriental company make), etc. can be used.
[0018]
[Table 2]

ナノチューブの分離膜による分離の一例

分離膜の孔径（μm）	分離される炭素固体	長さ（μm）
8．0	ナノチューブ	5以上
3．0	ナノチューブ	2～5
1．2	ナノチューブ	1～2
0．45	ナノチューブ	0．5～1
0．22	ナノチューブ	0．5以下
0．22μmの分離膜を通り抜けた濾液	ナノ粒子	0．1以下

[0019] 3) Make the sample which contains a nanotube nano particle in separation **** of the nanotube by ultra-centrifugal separation, and water suspend. At this time, carbon matter with comparatively large particle diameter other than a nanotube ino particle is removed with the glass filter. The cane-sugar water solution or cesium chloride water solution which gave the density gradient is put into a centrifuging tube, and a sample water solution is put on it. This centrifuging tube is put into a centrifugal separator, and it performs centrifugal. 96 hours performed 50000rpm from rotational frequency 500rpm (per minute 500 rotation), and centrifugal time amount for ultracentrifuge from 30 minutes The separated partition part is the approach of extracting carefully with a pipet, or the approach which carry out cooling freezing of the interior of a centrifuging tube by liquid nitrogen, and dissociate by cutting into round slices, and took out the sample from the centrifuging tube. For example, a nanotube and carbon matter other than a nano particle are first removed by the ultracentrifuge of a low speed (500rpm) and a short time (30 minutes), next a nanotube and a nano particle are separated by the ultracentrifuge of medium speed (1000rpm) Furthermore, if ultracentrifuge is performed for the nanotube isolated preparatively under a suitable engine speed and centrifugal time amount, a nanotube is separable with the difference between a diameter and die length. This result is shown in Table 3-1 and Table 3-2.
[0020]
[Table 3-1]

ナノチューブの超遠心による分離結果の例1
（超遠心回転数：５００ｒｐｍ，超遠心時間：３０分）

分取区分	分取される炭素物質
遠心管の底	無定形炭素
遠心管の底より上部上澄み液	ナノチューブ，ナノ粒子

[0021]
[Table 3-2]

ナノチューブの超遠心による分離結果の例２
（超遠心回転数：１０００ｒｐｍ，超遠心時間：３０分）

分取区分	分取される炭素物質	サイズ：直径と長さ
遠心管の底	ナノチューブ	５μｍ，１０ｎｍ以上
遠心管の底～上部１ｃｍの部分	ナノチューブ	５μｍ，１０ｎｍ以下
上部１ｃｍ以上の上澄み部分	ナノ粒子	２０ｎｍ（粒子径）以下

[0022]
4) The equipment used for the separation purification electrostatic separation by the electrical characteristics of a nanotube was made himself. This equipment consists of an exhauster 1, gas installation equipment 2, an electron beam or corona discharge equipment 3, a rotating drum 4, its circumference component and a control unit 5 for these moving part, a sample room 6, and separation sample acceptance rooms 7 and 8, as shown in drawing 1 . The sample to separate carries out degassing desiccation under an elevated temperature and a high vacuum preparatorily. The sample is put into the sample room 6, and it scatters on a rotating drum 4 at homogeneity. And an exposure or corona discharge shower of an electron beam is showered over a sample, and a drum 4 is rotated At this time, since the metal type nanotube is not charged, it is slid down into the sample acceptance room of right under in the place rotated 90 degrees. On the other hand, since the insulator type nanotube is charged, it does not draw and slide down into a drum by **** attraction. An insulating type nanotube fails to scratch a sample in the place which 270 degrees of drums rotated. If the above-mentioned actuation is successively repeated about the separated nanotubes of each, the high nanotube of degree of separation will be obtained more about electrical conductivity. The electrical conductivity of the nanotube divided into Table 4 is shown.
[0023]
[Table 4]
静電分離装置で分離されたナノチューブの電気伝導度

ナノチューブの種類	電気伝導度 ($\Omega^{-1}cm^{-1}$)
金属タイプ	約１＊１０^{2}
金属タイプ（５サイクル）	約１＊１０^{3}
金属タイプ（１０サイクル）	約５＊１０^{3}
絶縁体タイプ	約１＊１０$^{-1}$
絶縁体タイプ（５サイクル）	約１＊１０$^{-3}$
絶縁体タイプ（１０サイクル）	約１＊１０$^{-5}$

[0024]
5) Dissolve at all the nanotube obtained by the separation purification arc discharge of the nanotube using a surface active agent, and the product containing a nano particle in no solvent generally known. This property makes separation purification of a nanotube difficult. However, it is possible by adding a surface active agent to a solvent to solubilize a nanotube and a nano particle to a solvent. It is based on the ability of this solubilization to be distributed in a solvent as parent solvent colloid, when a nanotube, or a nano particle and a surfactant molecule forms a micell. Separation with a nano particle and other carbon matter is performed for a nanotube using solubilization of the nanotube by this surface active agent. If an example is

given, with water, dodecyl sulfonic-acid sodium (SDS) can be used as a surface active agent. Water 1000cm3 It receives, the sample containing a nanotube is paid for 100mg, and it is SDS 2x10-2 A mol (about 5.77g) is added and ultrasonic grinding is given. By removing the comparatively big carbon matter of particle diameter other than a nanotube and a nanotube with a glass filter, a sample melts into water completely as a hydrophile colloid. If suitable surface active agents, such as SDS, tree n-octyl phosphoretted hydrogen oxide, alkylbenzene-sulfonic-acid sodium, 2-sulfo succinic-acid dialkyl amide, alkyl trimethylammonium halide, the alkyl polyoxyethylene ether, fatty-acid polyhydric-alcohol ester, and p-alkylphenyl polyoxyethylene ether, are chosen, other solvents can solubilize a nanotube.
[0025] Moreover, as for macromolecule liquids, such as PORIBINI alcohol, itself has a property as a surfactant. Therefore, it is possible to distribute a nanotube and a nano particle as colloid, without adding other surface active agents in a giant-molecule liquid.
6) If the separation purification method of 1-5 is put together beyond the separation approach that combined the purification method to the above 1-5, it is possible to carry out separation purification of the nanotube more nearly alternatively. Next, it combines and some examples are given.
[0026] If the colloidal solution of a nanotube is prepared by the approach using the surface active agent of the above 6 and the purification method by ultrasonic grinding of 2 and membrane separation and the purification method by the column chromatography of 1 are put together, a nanotube is not only separable from other carbon matter, but it can carry out separation purification of the nanotube about magnitude and molecular weight. Furthermore, if the purification method of 1, 2, 3, and 5 is combined, selectivity will improve more.
[0027] If purification separation is performed by the approach using the electrical property of the nanotube of four after performing separation purification for a nanotube about magnitude and molecular weight using the purification method of the above 1, 2, and 3, a nanotube a uniform insulator type or metal type can be obtained about magnitude and molecular weight.
[0028]
[Effect of the Invention] By this invention, separation purification of the uniform good carbon nanotube can be carried out about molecular weight, magnitude, and electrical conductivity.

[Translation done.]

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